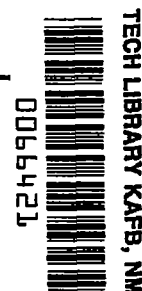


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# NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE 3634

CALCULATIONS OF THE RATE OF THERMAL  
DISSOCIATION OF AIR BEHIND NORMAL SHOCK WAVES AT  
MACH NUMBERS OF 10, 12, AND 14

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Washington  
April 1956

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## SUMMARY

The rate equation for the dissociation of air, based on simple-collision theory, and the numerical values of the factors that enter it are discussed. The rate equation and the conservation equations for a flowing dissociating gas are solved for the conditions (after the adjustment of vibration is taken into account) behind normal shock waves at Mach numbers of 10, 12, and 14. As a result, the process of thermal dissociation of air is shown from its initiation to its approach to equilibrium.

The results are applicable to a range of densities, and the Mach number range covers the temperature range between a temperature below which little dissociation occurs and a temperature above which electronic excitation and ionization may have to be taken into account. The distance required for a moderately large fraction of the oxygen to dissociate varies widely with Mach number and density, from a fraction of a millimeter to hundreds of meters. The dissociation of nitrogen, however, is too slow for much dissociation to occur within a minimum distance of about 20 meters. It has, therefore, been established that, granted the theory and the numerical constants used are accurate, the dissociation of nitrogen outside the boundary layer cannot have any significant aerodynamic effect at any altitude at Mach numbers less than 14.

## INTRODUCTION

The shock waves that will be produced by flight at the higher hypersonic speeds will result in high air temperatures that will cause at least a partial dissociation of the molecules of air into atoms. This dissociation represents a heat sink that might conceivably alleviate the problem of aerodynamic heating. On the other hand, the greater thermal conductivity of atoms or the release of heat by the recombination of atoms on the surface of the vehicle might aggravate the problem.

Because dissociation is not an instantaneous process but occurs at a finite rate, it follows that a thorough understanding of aerodynamic heating at hypersonic speeds requires some information on the rates of dissociation and of recombination. The present paper is concerned with calculations of the temporal and spatial rates of dissociation following normal shock waves and of the approach to dissociative equilibrium.

Other available calculations with regard to the rate of dissociation of air are those presented by Bethe and Teller (ref. 1). The present calculations differ from Bethe and Teller's in a number of respects. In the present paper, the dissociation process is followed from its initiation to its approach to equilibrium; whereas in reference 1, only the rates at various temperatures and the final conditions are given. Bethe and Teller do not show as such the variation of the degree of dissociation or the variation of the state variables with time or distance behind the shock wave. In the present paper, furthermore, the results of the calculations are so presented that they apply to a range of air densities; whereas in reference 1, only one density was used, and it was not very representative of the high altitudes at which hypersonic flight must occur. Other differences are that a somewhat different equation is used herein for the rate of dissociation, an equation is derived for the rate of recombination, and a significantly different value is used for the dissociation energy of nitrogen.

The present calculations are based on simple-collision theory. Because certain numerical factors cannot be evaluated by this theory but must be determined by experiment, and because no experiments on oxygen or nitrogen have been reported, values of these factors have been used that were based on consideration of the available experimental results with other gases. Because of the lack of direct experiment and because rates of dissociation may depend to some extent on quantum mechanical effects that are not taken into account by the simple-collision theory, the results of the present calculations should be considered to be uncertain within perhaps two orders of magnitude. This large degree of uncertainty is, however, in some cases not important - for example, in the case in which the calculations show that a significant degree of dissociation does not occur until the air has moved  $10^5$  meters behind the shock wave.

The calculations have been made for normal shock waves at Mach numbers of 10, 12, and 14, which cover most of the range between two temperatures. Below one temperature there is little dissociation, and above the other, electronic excitation and ionization may have to be taken into account. The free-stream temperature for all conditions was taken as  $300^\circ$  K.

Because adjustment of the specific heats of air to vibration of the molecules, following a thermal jump, is a much faster process than the

process of dissociation, the effects of this adjustment on the properties of the air and on the variables of state were calculated and taken into account as though they were complete before the process of dissociation began.

## SYMBOLS

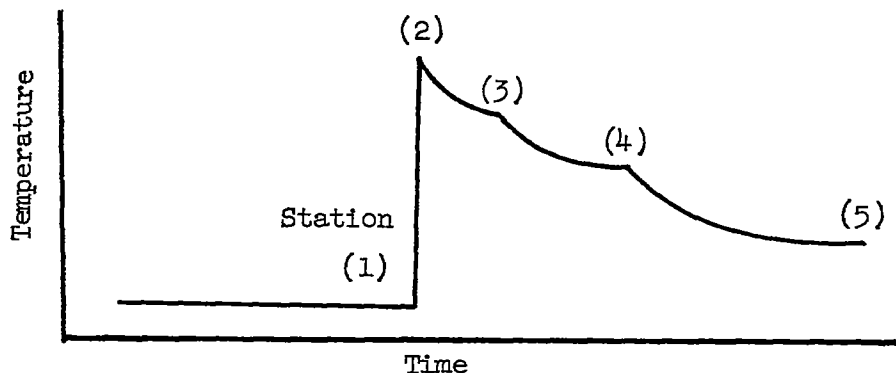
$a$	speed of sound, cm/sec
$A, B$	activation energies, ergs/mole
$c_1, c_2, c_3, c_4$	constants in the conservation equations
$D$	dissociation energy, ergs/mole
$F^0$	free energy, ergs/mole
$k$	Boltzmann's constant, $1.38 \times 10^{-16} \frac{\text{ergs}}{\text{molecule} \cdot ^\circ\text{K}}$
$k_d$	specific rate constant for dissociation, $\frac{\text{cm}^3}{\text{molecule} \cdot \text{sec}}$
$k_r$	specific rate constant for recombination, $\frac{\text{cm}^6}{\text{molecule}^2 \cdot \text{sec}}$
$K_c$	equilibrium constant, molecules/cm <sup>3</sup>
$K_p$	equilibrium constant, atm
$M$	molecular weight, gm/mole
$\bar{M}$	average molecular weight, gm/mole
$n_0$	Loschmidt's number, $2.687 \times 10^{19} \frac{\text{molecules}}{\text{atm} \cdot \text{cm}^3}$
$N_{Ma}$	Mach number
$N_0$	Avogadro's number, $6.02 \times 10^{23} \frac{\text{molecules}}{\text{mole}}$
$P$	pressure, dynes/cm <sup>2</sup>

P	steric factor
R	gas constant, $8.31 \times 10^7 \frac{\text{ergs}}{\text{mole-}^\circ\text{K}}$
t	time, sec
T	temperature, $^\circ\text{K}$
u	velocity, cm/sec
U	unspecified molecule or atom
Z	collision rate, $\frac{\text{collisions}}{\text{cm}^3\text{-sec}}$
$\beta$	energy content per molecule divided by $kT$
$\beta'$	energy content per gram divided by $p/\rho$
$\gamma$	ratio of specific heats
$\bar{\gamma}$	average value of ratio of specific heats
$\mu$	reduced molecular weight, gm/mole
$\rho$	mass density, gm/cm <sup>3</sup>
$\sigma$	molecular diameter, cm
$\tau$	duration of collision, sec
( )	concentration, molecules/cm <sup>3</sup>
Subscripts:	
1	free-stream station
2	station behind shock wave where translation and rotation are in equilibrium
3	station behind shock wave where vibration is in equilibrium
4	station behind shock wave where dissociation of oxygen is in equilibrium

- 5 station behind shock wave where dissociation of nitrogen  
is in equilibrium
- o initial, except for Avogadro's number and Loschmidt's number

## THEORY

When air passes through a strong shock wave, there follows a conversion of energy of directed translational motion into other manifestations of energy, such as random translation, rotation, vibration, and dissociation. Because the temperature of a gas depends on the energy of random translation, when energy is transferred into this manifestation, the temperature of the gas rises. If, at a subsequent time, a portion of the energy of random translation is converted into other modes, the temperature falls. Because of differences in the magnitudes of the time required for the various processes to absorb their equilibrium amounts of energy, considering them to occur separately and consecutively results in a good approximation. The variation of temperature from its free-stream value to its value following establishment of thermal equilibrium can, therefore, be represented as in the following schematic diagram, in which different (and nonlinear) scales are used between different stations:



Station (1) represents conditions in the free stream ahead of the shock wave where the temperature is low enough ( $300^{\circ}$  K for the present calculations) that vibration of the molecules is not appreciably excited. Rotation of the molecules is, however, completely excited, and the value of the ratio of the specific heats  $\gamma$  is 1.4. Station (2) represents conditions behind but very close to the shock wave where translation and rotation are again in equilibrium, but vibration is just beginning to be excited. At station (3), vibration is fully established, but dissociation to a first approximation is only beginning. At station (4), sufficient time has elapsed for the dissociation of oxygen to reach

equilibrium; and at station (5), the dissociation of nitrogen is in equilibrium and the temperature has reached its equilibrium value.

#### Adjustment of Translation and Rotation

Station (2) represents conditions behind but very close to the shock wave. The thermal jump across the shock wave throws the translational and rotational degrees of freedom temporarily out of equilibrium, but only a few collisions are sufficient to establish equilibrium not only of the translational but also of the rotational degrees of freedom (ref. 1). Station (2) then is taken to be only a few mean free paths behind the front of the shock wave. Although the temperature at station (2) is high enough for the vibrational degrees of freedom to be excited, sufficient time (or a sufficient number of collisions) has not passed for them to be appreciably excited, and the ratio of the specific heats remains at 1.4.

Conditions at station (2) are, therefore, calculable by the Rankine-Hugoniot equations for a normal shock wave as

$$\left. \begin{aligned} \frac{T_2}{T_1} &= \frac{(1.4N_{Ma,1}^2 - 0.2)(0.2N_{Ma,1}^2 + 1)}{(1.2N_{Ma,1})^2} \\ \frac{u_1}{u_2} = \frac{\rho_2}{\rho_1} &= \frac{1.2N_{Ma,1}^2}{1 + 0.2N_{Ma,1}^2} \\ \frac{p_2}{p_1} &= \frac{7}{6} N_{Ma,1}^2 - \frac{1}{6} \\ N_{Ma,2}^2 &= \frac{N_{Ma,1}^2 + 5}{7N_{Ma,1}^2 - 1} \end{aligned} \right\} \quad (1)$$

#### Adjustment of Vibration

Adjustment of the vibrational degrees of freedom occurs between stations (2) and (3). This process requires a number of collisions (or a time or distance) that is large compared with that required for adjustment of translation and rotation, but is small compared with that required for establishment of dissociative equilibrium. As discussed extensively in reference 1, the number of collisions required for the establishment of vibrational equilibrium of oxygen and nitrogen molecules is very

difficult to establish accurately on the basis of the current state of theory and experiment. The estimated values are such (100 at high temperatures), however, that the time required is much less than that required for dissociation, and neither the time nor the distance required is discussed further in the present paper. The conditions at station (3) must be calculated, however, before calculations can be made of the rate of dissociation.

The change in conditions between stations (2) and (3) is herein considered to occur in a single step, and conditions at station (3) are calculated from those at station (2) by means of the three conservation equations. At station (2), five degrees of freedom  $f$  are active, and the ratio of specific heats is

$$\gamma = \frac{f + 2}{f} = 1.4 \quad (2)$$

Since, at this station,  $d\beta'/dT$  is zero,

$$\beta' = \frac{\gamma}{\gamma - 1} = 3.5 \quad (3)$$

At station (3), if there were no effects of electronic excitation, anharmonicity of vibration, interaction between rotation and vibration, and stretching due to the centrifugal effects of rotation, the value of  $\beta'$  would be 4.5. Reference 2 shows, however, that, over the range of temperature involved herein, the average value of  $\beta'$  for the nitrogen molecule is about 4.6 and for the oxygen molecule is about 4.9. Accordingly, a value of 4.7 for air was adopted for use herein.

The equations for conservation of energy, mass, and momentum between stations (2) and (3) are then, respectively,

$$4.7 \frac{p_3}{\rho_3} + \frac{u_3^2}{2} = 3.5 \frac{p_2}{\rho_2} + \frac{u_2^2}{2} = c_1 \quad (4)$$

$$\rho_3 u_3 = \rho_2 u_2 = c_2 \quad (5)$$

$$p_3 + \rho_3 u_3^2 = p_2 + \rho_2 u_2^2 = c_3 \quad (6)$$

These three equations can be solved for  $\rho_3$ . From equations (4) and (5),

$$4.7 p_3 \rho_3 + 0.5 c_2^2 = c_1 \rho_3^2 \quad (7)$$



From equations (5) and (6),

$$4.7p_3\rho_3 + 4.7c_2^2 = 4.7c_3\rho_3 \quad (8)$$

From equations (7) and (8),

$$c_1\rho_3^2 - 4.7c_3\rho_3 + 4.2c_2^2 = 0$$

and

$$\rho_3 = \frac{4.7c_3 + \sqrt{(4.7c_3)^2 - 16.8c_1c_2^2}}{2c_1} \quad (9)$$

(Only the positive sign should be used ahead of the root in order that the second law of thermodynamics not be violated.)

The velocity  $u_3$  is then given by equation (5) and the pressure  $p_3$  by equation (6) or equation (4). The temperature  $T_3$  is given by the general gas law

$$p_3 = \frac{R}{M} \rho_3 T_3 \quad (10)$$

in which the molecular weight  $M$  is 28.8 gm/mole.

#### Rate Equations for Dissociation

The principal purpose of the present paper is to calculate conditions (as functions of time and distance) between stations (3) and (5). In order to make these calculations, it is necessary to have (1) an expression for the rate at which dissociation occurs, (2) an expression for the rate at which recombination occurs, and (3) equations that express conservation of energy, mass, and momentum. The present section is devoted to a derivation of the rate equation for dissociation and to a discussion of the choice of numerical values for the quantities that appear in that equation.

The simple physical picture of dissociation that is employed herein is that the gas is composed of diatomic molecules, that the two atoms of each molecule are held together by a rather strong binding force, and that at station (1), ahead of the shock wave, the temperature of the gas is low and the kinetic energy of random motion of the molecule is small enough that only a very negligible portion of the molecules is dissociated.

At station (3), where the temperature of the gas has been raised considerably by passage through a shock wave, the energy of random translational motion has been increased enough that a nonnegligible degree of dissociation is possible, because in an appreciable fraction of the collisions the kinetic energy involved is great enough that a collision can result in breaking of the binding force and in the separation of a molecule into two atoms.

The present calculations of the rate of dissociation have been based on simple-collision theory. The only other theory that might be considered is the activated-complex theory of absolute reaction rates of Eyring and others (ref. 3). Use of this theory, however, was not practicable because the potential-energy surfaces that are required apparently have not yet been calculated for oxygen or nitrogen. A fundamental weakness of the collision theory is that complicated rate processes that involve important quantum mechanical effects cannot accurately be described or predicted except by quantum mechanical or wave mechanical theory. Whether the dissociation of oxygen and nitrogen involves important quantum mechanical effects is not yet known. At any rate, these effects, if present, would not be taken into account by the simple-collision theory. The results of calculations of rates by this theory can, therefore, not be depended upon to be accurate within some factor that may be as large as one or two orders of magnitude.

The collision theory postulates that the rate at which molecules are dissociated into atoms depends on the rate at which collisions occur in which sufficient energy is transferred. The rate of dissociation is customarily calculated as the product of three factors: (1) the rate at which binary collisions occur, (2) the fraction of these collisions in which sufficient energy is involved, and (3) the fraction of collisions involving sufficient energy that actually results in dissociation.

The first of these factors, the rate at which binary collisions occur, need not be derived herein, as the derivation is straightforward and is given in several textbooks on the kinetic theory of gases, on statistical mechanics, and on gaseous reactions. The rate, in  $\frac{\text{collisions}}{\text{cm}^3\text{-sec}}$ , at which binary collisions occur between  $\text{O}_2$  and U molecules, for example, is

$$Z_{\text{O}_2} = \frac{2}{(1,2)} (\text{O}_2)(\text{U}) \left( \frac{\sigma_{\text{O}_2} + \sigma_{\text{U}}}{2} \right)^2 (2\pi RT)^{1/2} \left( \frac{M_{\text{O}_2} + M_{\text{U}}}{M_{\text{O}_2} M_{\text{U}}} \right)^{1/2} \quad (11)$$

The symmetry factor (1,2) is equal to 1 if the two colliding molecules are of different species and is equal to 2 if they are of the same

species. Immediately behind the shock wave, 79 percent of the U. molecules are nitrogen molecules and 21 percent are oxygen molecules. As dissociation proceeds, the percentage of molecules decreases (oxygen decreases faster than nitrogen) and the percentage of atoms increases. The diameters and the molecular weights of the atoms differ from those of the molecules. The procedure adopted herein is not to write average values of concentration, diameter, and molecular weight for each stage of the process but to include in the equation a separate term for each constituent of the gas. Furthermore, inasmuch as rates of collision of both oxygen molecules and nitrogen molecules with all species of particles are needed, separate equations are written for oxygen and for nitrogen:

$$\begin{aligned}
 Z_{O_2} = & (O_2)^2 (\sigma_{O_2})^2 (2\pi RT)^{1/2} \left( \frac{2}{M_{O_2}} \right)^{1/2} + \\
 & 2(O_2)(O) \left( \frac{\sigma_{O_2} + \sigma_O}{2} \right)^2 (2\pi RT)^{1/2} \left( \frac{M_{O_2} + M_O}{M_{O_2} M_O} \right)^{1/2} + \\
 & 2(O_2)(N_2) \left( \frac{\sigma_{O_2} + \sigma_{N_2}}{2} \right)^2 (2\pi RT)^{1/2} \left( \frac{M_{O_2} + M_{N_2}}{M_{O_2} M_{N_2}} \right)^{1/2} + \\
 & 2(O_2)(N) \left( \frac{\sigma_{O_2} + \sigma_N}{2} \right)^2 (2\pi RT)^{1/2} \left( \frac{M_{O_2} + M_N}{M_{O_2} M_N} \right)^{1/2} \quad (12)
 \end{aligned}$$

$$\begin{aligned}
 Z_{N_2} = & 2(N_2)(O_2) \left( \frac{\sigma_{N_2} + \sigma_{O_2}}{2} \right)^2 (2\pi RT)^{1/2} \left( \frac{M_{N_2} + M_{O_2}}{M_{N_2} M_{O_2}} \right)^{1/2} + \\
 & 2(N_2)(O) \left( \frac{\sigma_{N_2} + \sigma_O}{2} \right)^2 (2\pi RT)^{1/2} \left( \frac{M_{N_2} + M_O}{M_{N_2} M_O} \right)^{1/2} + \\
 & (N_2)^2 (\sigma_{N_2})^2 (2\pi RT)^{1/2} \left( \frac{2}{M_{N_2}} \right)^{1/2} + \\
 & 2(N_2)(N) \left( \frac{\sigma_{N_2} + \sigma_N}{2} \right)^2 (2\pi RT)^{1/2} \left( \frac{M_{N_2} + M_N}{M_{N_2} M_N} \right)^{1/2} \quad (13)
 \end{aligned}$$

The first of several difficulties or uncertainties to be encountered in the present calculations is now apparent: the exact numerical values to be assigned to the molecular diameters are not known. The kinetic theory of gases enables the effective collision diameter for the various transport phenomena to be calculated from experimental measurements: for transfer of momentum, from measurements of viscosity; for transfer of energy, from measurements of thermal conductivity; and for transfer of mass, from measurements of rate of diffusion. The results by various methods do not agree exactly, but usually agree within approximately 10 percent. Kennard (ref. 4) regards the results from viscosity as probably the most reliable data with regard to collision diameters. For this and other reasons to be given presently, the values of  $\sigma$  obtained by this method for molecular oxygen and nitrogen have been used in the present investigation. The values of  $\sigma$  taken from Chapman and Cowling (ref. 5) are

$$\sigma_{O_2} = 3.6 \times 10^{-8} \text{ centimeter}$$

$$\sigma_{N_2} = 3.8 \times 10^{-8} \text{ centimeter}$$

The data listed by Chapman and Cowling also show that the following trends are approximately true: For a monatomic gas,  $\sigma$  is about 75 percent as large as the  $\sigma$  for a diatomic gas of the same molecular weight; and for a monatomic gas,  $\sigma$  is about 75 percent as large as the  $\sigma$  for another monatomic gas of twice the molecular weight. On the basis of these trends, the molecular diameters for oxygen and nitrogen were chosen for use here as

$$\sigma_O = 2.0 \times 10^{-8} \text{ centimeter}$$

$$\sigma_N = 2.1 \times 10^{-8} \text{ centimeter}$$

The following reservations with regard to the choices of  $\sigma$  should be noted. In the first place, the use of a value of  $\sigma$  calculated from measurements of viscosity, which is a momentum-transfer process, can scarcely be wholly justified in energy-transfer processes. In the second place,  $\sigma$  may be a function of relative velocities and, consequently, of temperature. However, the function is unknown because the exact variation of molecular forces with distance that should be used in calculating  $\sigma$  from measurements of viscosity is not known. (The model used in ref. 5 for calculating  $\sigma$  was a smooth, rigid, elastic sphere.) One might consider, for example, using Sutherland's model for calculating  $\sigma$ , but one could not really wholly justify such a refinement.

The second of the factors that make up the expression for the rate of dissociation is the fraction of collisions in which sufficient energy is involved. (Sufficient energy means energy equal to or greater than the dissociation energy  $D$ .) A diatomic molecule has energy of translation, rotation, and vibration. Dissociation occurs when the vibrational energy exceeds a certain value. However, the simple-collision theory does not tell which of the three forms of energy (or what combination of them) is important or effective in regard to transfer of energy to vibration of one of the two colliding molecules. In fact, it is customary (as is done herein) to ignore the rotational and the vibrational energies of the colliding molecules and to consider only their translational energy. Even so, another difficulty remains. Two postulates are still clearly possible: one, that the total kinetic energy due to the relative motion of the two molecules shall exceed a specified value  $D$ , and the other, that the kinetic energy due only to the relative motion along the line of centers at the moment of impact shall exceed  $D$ . The second of these postulates is the one that is usually used in calculations of gaseous reactions. As many textbooks show, the Boltzmann factor  $e^{-D/RT}$  gives the fraction of all binary collisions in which  $D$  is equal to or less than the kinetic energy of translation due to the component of relative motion that lies along the direction of the line of centers at the moment of collision. This is the factor that is used in the present calculations. The first postulate leads to the factor  $\left(\frac{D}{RT} + 1\right)e^{-D/RT}$  as the fraction of collisions in which the energy of translation is sufficient to cause dissociation. Reference 1 used this factor with the "1" omitted as a simplification.

There are two reasons why the simple Boltzmann factor  $e^{-D/RT}$  was used in the present investigation, in addition to the fact that it is usually used. One reason is that, when the relative velocity of translation of two molecules is broken down into two components, one along the line of centers at the moment of collision and the other perpendicular to that direction, it appears that the velocity perpendicular to the line of centers affects principally the angular momentum, or mutual rotation, of the two molecules; consequently, only the other component of velocity might affect the vibration of one of the molecules.

The other reason for the use of the Boltzmann factor is now to be developed. Usually, or perhaps always, an additional condition is made that there is only a probability  $P$  and not a certainty that dissociation will occur in the fraction of collisions in which the energy requirement is met. This condition is based on the assumption that, in order for the translational energy of one of the colliding molecules to be transferred into vibrational energy, some of the possible relative orientations of the two molecules are more effective than others. This probability  $P$  is, therefore, called the steric factor. There is no way of estimating  $P$  on the basis of simple-collision theory, so reliance must be placed in experiment. No experiments, however, have been reported on the thermal

dissociation of oxygen or nitrogen. As a matter of fact, experiments do not actually give a value for  $P$  but only for the product  $P\sigma^2$ . Reference 6 states that experimental data on the rates of approximately six homogeneous, bimolecular, second-order, gaseous reactions can be correlated by the simple-collision theory if the second of the two postulates about kinetic energy is accepted (reaction occurs only in those collisions in which the kinetic energy due to relative motion along the line of centers equals or exceeds  $D$ ), if molecular diameters of the order of a few angstroms (that is, of the order of those obtained from viscosity measurements) are used, and if the steric factor is taken close to unity.

Furthermore, reference 7 (pp. 170 and 171) shows that, for several bimolecular reactions, the steric factor  $P$  has a value given approximately by the ratio of the observed rate of reaction  $a$  to the calculated rate of reaction  $b$  when the calculations are based on the Boltzmann factor, and where

$$5 \times 10^{13} < a < 5 \times 10^{14}$$

$$1 \times 10^{14} < b < 6 \times 10^{14}$$

A rough approximation to the average value of  $P$  from this information is between  $1/3$  and  $1$ . For the present calculations, therefore, the Boltzmann factor was used, the molecular diameters based on viscosity measurements were used, and the value of  $P$  was taken as  $1/2$ .

A numerical comparison of the values used in this paper with those of reference 1 might be of interest. The present considerations have the rate of dissociation of oxygen proportional to  $P = 0.5$ . Bethe and Teller have the rate proportional to  $PD/RT$  where  $P = 0.01$ .

$T$ , °K	$P$ (present paper)	$PD/RT$ (ref. 1)
4,000	0.5	0.15
8,000	.5	.08

The comparison shows that the rate used in the present calculations is several times greater than that used in reference 1.

The numerical values of the dissociation energies that were chosen for the present calculations are the latest available and are probably the best values. The dissociation energy of oxygen has long been accepted as 117,200 calories per mole. A better value now appears to be 117,960 calories per mole (ref. 8), and that value was used herein. The dissociation

energy of nitrogen has long been uncertain. In reference 1, a value of 182,000 calories per mole was used. Recent evidence (refs. 9 to 12) indicates that the most probable value is 225,100 calories per mole, and that value was used in the present calculations.

The rate at which dissociation occurs, in  $\frac{\text{molecules}}{\text{cm}^3\text{-sec}}$  is given by the product of the rate at which binary collisions occur  $Z$  and the ratio of dissociations to collisions  $P e^{-D/RT}$ . Thus,

$$-\frac{d(O_2)}{dt} = Z_{O_2} P e^{-D_{O_2}/RT} \quad (14)$$

and

$$-\frac{d(N_2)}{dt} = Z_{N_2} P e^{-D_{N_2}/RT} \quad (15)$$

If the values of  $Z$  as given by equations (12) and (13) are used, numerical values are substituted for the various constants, and arithmetical simplifications are made, the rate equations (14) and (15) become

$$-\frac{d(O_2)}{dt} = \left[ 3.25(O_2) + 4.79(O) + 7.1(N_2) + 5.19(N) \right] 1.15 \times 10^{-12} (O_2) \sqrt{T} e^{-59400/T} \quad (16)$$

and

$$-\frac{d(N_2)}{dt} = \left[ 7.1(O_2) + 5.27(O) + 3.85(N_2) + 5.71(N) \right] 1.15 \times 10^{-12} (N_2) \sqrt{T} e^{-113340/T} \quad (17)$$

#### Rate Equations for Recombination

The purpose of the present section is to derive equations for the rate of recombination of atoms into molecules. These equations will be used for comparing the ratio of the rates of dissociation and recombination with the equilibrium constant.

When two atoms combine, a stable molecule is formed only if a portion of the binding energy is removed by a third body and if momentum is conserved. In other words, triple collisions are necessary for the recombination of atoms into diatomic molecules. In order to calculate the rate at which recombination of atoms occurs, the postulate is made that recombination can occur in two ways. Two atoms can collide and if, during their collision, a third body collides with them, recombination may occur. Or, an atom and a third body can collide and if, during their collision, another atom collides with them, recombination of the two atoms may occur.

The method of calculation used herein is based on the idea that triple collisions can be considered as binary collisions between, on the one hand, a colliding pair of particles and, on the other hand, a third particle. An equation similar to equation (11) can be written for rate of collisions. Then, multiplication by the ratio of recombinations to collisions (product of steric factor and Boltzmann factor) gives as the rate in  $\frac{\text{molecules}}{\text{cm}^3\text{-sec}}$  of recombination of oxygen atoms, for example,

$$\begin{aligned} \frac{d(O_2)}{dt} = & 2(OO)(U) \left( \frac{\sigma_{OO} + \sigma_U}{2} \right)^2 (2\pi RT)^{1/2} \left( \frac{M_{OO} + M_U}{M_{OO}M_U} \right)^{1/2} P_{OO \cdot U} e^{-A/RT} + \\ & 2(OU)(O) \left( \frac{\sigma_{OU} + \sigma_O}{2} \right)^2 (2\pi RT)^{1/2} \left( \frac{M_{OU} + M_O}{M_{OU}M_O} \right)^{1/2} P_{OU \cdot O} e^{-B/RT} \quad (18) \end{aligned}$$

Here, (OO) represents the concentration of pairs of O atoms that are in the act of colliding with each other; and (OU), the concentration of O and U particles that are in the act of colliding with each other. The steric factor  $P_{OO \cdot U}$  is a measure of the efficiency of U as a remover of energy and momentum from a pair of O atoms, and  $P_{OU \cdot O}$  is a measure of the efficiency of U in removing energy and momentum when U is already in temporary collision with an O atom and the pair is hit by another O atom. The quantities A and B are activation energies: the reaction will not occur if the energies involved do not equal or exceed the activation energy.

Of course, equation (18) is useless until the concentrations of colliding particles (OO) and (OU) are determined. These concentrations will be considered as equal to the rate at which the collisions occur multiplied by the mean duration of a collision. Thus,

$$(OO) = \tau_{OO} Z_{OO}$$

$$(OU) = \tau_{OU} Z_{OU}$$



By use of an equation similar to equation (11), the following equations result:

$$(OO) = \tau_{OO}(O)(O)\sigma_0^2(2\pi RT)^{1/2}\left(\frac{2}{M_O}\right)^{1/2} \quad (19)$$

and

$$(OU) = 2\tau_{OU}(O)(U)\left(\frac{\sigma_0 + \sigma_U}{2}\right)^2(2\pi RT)^{1/2}\left(\frac{M_O + M_U}{M_O M_U}\right)^{1/2} \quad (20)$$

These equations are considered to give the average concentration of particles engaged in binary collisions at any given instant.

When (OO) and (OU) as given by equations (19) and (20) are substituted into equation (18), the result is

$$\begin{aligned} \frac{d(O_2)}{dt} = & 2(O)(O)(U)\sigma_0^2\left(\frac{\sigma_{OO} + \sigma_U}{2}\right)^2(2\pi RT)\left(\frac{2}{M_O}\right)^{1/2}\left(\frac{M_{OO} + M_U}{M_{OO}M_U}\right)^{1/2}P_{OO \cdot U}\tau_{OO}e^{-A/RT} + \\ & 4(O)(O)(U)\left(\frac{\sigma_0 + \sigma_U}{2}\right)^2\left(\frac{\sigma_{OU} + \sigma_O}{2}\right)^2(2\pi RT)\left(\frac{M_O + M_U}{M_O M_U}\right)^{1/2}\left(\frac{M_{OU} + M_U}{M_{OU}M_O}\right)^{1/2}P_{OU \cdot O}\tau_{OU}e^{-B/RT} \end{aligned} \quad (21)$$

A similar equation can be written for the rate of recombination of nitrogen atoms. Subsequent to the derivation of these equations, it was learned that Herzfeld (ref. 13) had used the same concept. Apparently, it has been customary usually to modify Herzfeld's ideas and to consider collisions between the third body and each of the two particles that are in temporary collision with each other rather than to consider collisions between the third body and the complex as a whole which has been formed by the two colliding particles. Possibly, the reason has been that it was thought easier to estimate the collision diameter of an atom than that of two colliding atoms. This usual modification has not been followed herein; this is one reason that the equations used herein are slightly different from those given in the literature. (See for example, refs. 7 (p. 177), 14 (p. 78), 15, and 16.)

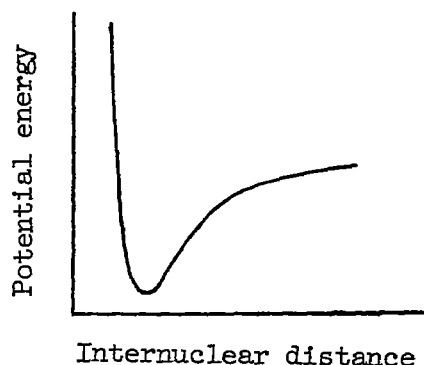
Still unevaluated are the activation energies A and B, the steric factor P, and the collision duration  $\tau$ . Because the potential-energy curve for oxygen, which is well established, indicates that A is zero for oxygen, and because no reason is known why they should be large enough to have a significant effect, A and B are assumed to be zero. On the basis of experiments on the recombination of bromine atoms discussed in reference 14 (pp. 177 and 248), the steric factors for that reaction

appear to be of the order of 0.01. On the basis of experiments on recombination discussed in reference 7 (pp. 179 and 180), the steric factors appear to have values much closer to unity. The experiments on the recombination of iodine atoms reported in reference 16 indicate average values for that reaction of approximately 0.25. For the present study, a value of 0.1 was chosen for both  $P_{OO.U}$  and  $P_{OU.O}$ .

The mean duration of a collision can be defined as twice the quotient of the range of the intermolecular forces and the mean speed of random translation. In accordance with the discussion in reference 1, a value of  $3 \times 10^{-9}$  centimeter has been used herein for the range of the forces. The average speed is shown in the textbooks to be  $(8RT/\pi\mu)^{1/2}$  cm/sec. Therefore,

$$\tau = 6 \times 10^{-9} \left( \frac{\pi\mu}{8RT} \right)^{1/2} \text{ seconds} \quad (22)$$

No attempt is made herein to defend the apparent inconsistency of using a much larger value for the molecular radius  $\sigma/2$  than for the range of intermolecular forces. The fact that  $\tau$  as given by equation (22) probably has about the right order of magnitude ( $10^{-14}$  to  $10^{-13}$  second) can, however, be indicated by a different method. Consider that two atoms approach each other and that their potential energy follows the curve shown in the sketch:



After one vibration, the atoms will again separate, unless their excess energy is removed by a third body. The duration of their conjunction then cannot exceed one period of vibration, which is about  $10^{-14}$  to  $10^{-13}$  second. It should be emphasized, however, that the value given by equation (22) is an approximation and can probably be wrong by an order of magnitude.

The effective diameters of the temporary particles formed by the binary collisions were taken as 88 percent of the sum of the diameters of the two colliding particles in order to give diameters that were equal to those of oxygen and nitrogen molecules. Thus,

$$\sigma_{OO} = 3.6 \times 10^{-8} \text{ centimeter}$$

$$\sigma_{OO_2} = 5.0 \times 10^{-8} \text{ centimeter}$$

$$\sigma_{ON} = 3.7 \times 10^{-8} \text{ centimeter}$$

$$\sigma_{ON_2} = 5.2 \times 10^{-8} \text{ centimeter}$$

$$\sigma_{NO_2} = 5.1 \times 10^{-8} \text{ centimeter}$$

$$\sigma_{NN} = 3.8 \times 10^{-8} \text{ centimeter}$$

$$\sigma_{NN_2} = 5.3 \times 10^{-8} \text{ centimeter}$$

When substitution is made in the rate equation (21) for  $\tau$  from equation (22), substitutions of numerical values are made for the constants, and numerical simplifications are made, then the equation for the rate of recombination of oxygen atoms in molecules becomes the following equation:

$$\frac{d(O_2)}{dt} = 1.73 \times 10^{-36} T^{1/2} (O)^2 \left[ 17.1(O_2) + 2.4(O) + 19.5(N_2) + 7.6(N) \right] \quad (23)$$

Equation (24) is a similar equation, similarly derived, for the recombination rate of nitrogen atoms:

$$\frac{d(N_2)}{dt} = 1.73 \times 10^{-36} T^{1/2} (N)^2 \left[ 19.8(O_2) + 8.6(O) + 22.6(N_2) + 3.1(N) \right] \quad (24)$$

## Comparison of Equilibrium Constants

A partial check on the rate equations can be made by comparing the value of the ratio of the specific rate constants with the value of the equilibrium constant as calculated by statistical mechanics.

A specific rate constant  $k_d$  for the dissociation of oxygen can be defined by the equation

$$-\frac{d(O_2)}{dt} = k_d(O_2)(U)$$

A specific rate constant  $k_r$  for the recombination of oxygen can be defined by the equation

$$\frac{d(O_2)}{dt} = k_r(O)^2(U)$$

If, for simplicity, only pure oxygen is considered, equations (16) and (23) indicate, respectively, that each rate can be written as the sum of two rates. Thus,

$$k_d(O_2)(U) = k_{d,1}(O_2)^2 + k_{d,2}(O_2)(O)$$

and

$$k_r(O)^2(U) = k_{r,1}(O)^2(O_2) + k_{r,2}(O)^3$$

When the degree of dissociation is large, the first term on the right-hand side of each of the two preceding equations is small compared with the second term. Therefore, to a good approximation,

$$\frac{k_d}{k_r} = \frac{k_{d,2}}{k_{r,2}}$$

At equilibrium, moreover, the rates of dissociation and recombination are equal, and, accordingly,

$$\frac{k_d}{k_r} = \frac{(O)^2}{(O_2)}$$

But  $(O)^2/(O_2)$  is just the equilibrium constant  $K_C$ . The more commonly used equilibrium constant  $K_p$  is related to  $K_C$  by the equation

$$K_p = \frac{T}{273n_O} K_C$$

Therefore,

$$K_p = \frac{T}{273n_O} \frac{k_{d,2}}{k_{r,2}}$$

and, by use of equations (16) and (23),

$$K_p = \frac{181T}{e^{59400/T}}$$

Thermodynamics shows that  $K_C = e^{-\Delta F^0/RT}$ . The change in free-energy  $\Delta F^0$  can be calculated from spectroscopic information by means of statistical mechanics. An independent partial check, of sorts, on the presently derived rate equations is, therefore, possible by comparing the value of  $K_p$  obtained from the calculated change in free energy and tabulated in reference 17 with the value of  $K_p$  obtained from the ratio of the specific rate constants. A comparison is made in table I. (The values taken from ref. 17 were adjusted to take into account the different value of the dissociation energy of oxygen used herein.)

The last column of the table shows that the ratio of the specific rate constants for oxygen needs to be increased by a factor of 6:1 to 8:1 for agreement with the equilibrium constant, and for nitrogen by a factor of 9:1. The factor is actually smaller than might be expected. In reference 18, for example, a factor of about 100 was needed in the ratio of the rate of dissociation of iodine and of bromine gas calculated by collision theory to the rate of recombination determined experimentally by E. Rabinowitch and W. C. Wood for the equilibrium constant so determined to agree with the known values of the equilibrium constant. In reference 19, a similar comparison was made in which new data on the rate of recombination of iodine atoms were used, and a similar factor (of about 100 or more) was found to be needed for agreement. (These results may possibly serve as additional evidence that the steric factor used in ref. 1 was much too small.)

Although the factor of 6:1 to 9:1 that is required in the ratio of the present rate constants may appear to be reasonably small, the fact

should be borne in mind that this factor does not necessarily represent the uncertainty in the rate constants themselves or in equations (16), (17), (23), and (24). The rate constants and the rate equations may be in error by much larger factors, the errors being partially canceled when the ratio is taken.

### Flow Equations for Dissociation Process

At station (3) (see sketch on p. 5), the dissociation process begins, and at station (5) it has closely approached equilibrium. Although it can be shown that at equilibrium the state of a gas does not depend on the rate of approach to equilibrium (see ref. 1), at any station  $x$  between stations (3) and (5) the state of the gas does depend on the degree of dissociation at that station. Because the gas is assumed to be flowing and not stationary, calculations of its state at any station  $x$  are to be made not only by use of the rate equations (16), (17), (23), and (24), but also by use of flow equations based on conservation of mass, momentum, and energy. Such equations are developed in the present section.

The general gas law for partially dissociated air is

$$p = \frac{R}{\bar{M}} \rho T \quad (25)$$

where

$$\bar{M} = \frac{28(N_2) + 14(N) + 32(O_2) + 16(O)}{(N_2) + (N) + (O_2) + (O)} \quad (26)$$

and

$$\rho = \frac{1}{N_O} [28(N_2) + 14(N) + 32(O_2) + 16(O)] \quad (27)$$

The equation that expresses conservation of the ratio of number of nitrogen atoms to number of oxygen atoms, whether the atoms are free or combined, is

$$2(N_2) + (N) = \frac{79}{21} [2(O_2) + (O)] \quad (28)$$

Conservation of mass gives

$$\rho u = \rho_3 u_3 = c_2 \quad (29)$$

The integrated form of the equation of motion is

$$p + \rho u^2 = p_3 + \rho_3 u_3^2 = c_3 \quad (30)$$

The equation for conservation of energy is not so easily written down but must be derived, as is done in the following discussion. For example, if  $\beta_{N_2} kT$  is the energy content of a molecule of nitrogen, the internal energy in the nitrogen molecules in unit volume of air is  $\beta_{N_2} kT(N_2)$  and the total internal-energy content of air is, in ergs/cm<sup>3</sup>,

$$kT [\beta_{N_2}(N_2) + \beta_N(N) + \beta_{O_2}(O_2) + \beta_O(O)]$$

(The notation used herein differs from that in reference 2. The quantity  $\beta_{N_2}$ , as used herein, has the same meaning as  $\beta(N_2)$  in ref. 2.) As ordinarily conceived, the equation for conservation of energy is written in terms of unit mass of fluid. Division of the preceding expression by  $\rho$  then gives the internal energy content per gram of air:

$$\frac{RT [\beta_{N_2}(N_2) + \beta_N(N) + \beta_{O_2}(O_2) + \beta_O(O)]}{28(N_2) + 14(N) + 32(O_2) + 16(O)}$$

The sum of the internal energy of a gram of fluid and its kinetic energy of directed motion  $u^2/2$  must be constant at all station, except for the energy that goes into dissociating the gas molecules, and provided that the external work done on the gas is included in the "internal energy" and the work of dissociation is not so included. The energy that is absorbed in dissociating the nitrogen in a unit mass of gas can be seen to be

$$\frac{D_{N_2}(N)}{2\rho N_O}$$

With this dissociation energy taken into account and with the aforementioned specification of the meaning of  $\beta$ , the energy balance equation is

$$\frac{RT [\beta_{N_2}(N_2) + \beta_N(N) + \beta_{O_2}(O_2) + \beta_O(O)]}{28(N_2) + 14(N) + 32(O_2) + 16(O)} + \frac{u^2}{2} + \frac{D_{N_2}(N) + D_{O_2}(O)}{2 [28(N_2) + 14(N) + 32(O_2) + 16(O)]} = \frac{RT [\beta_{N_2}(N_2)_3 + \beta_{O_2}(O_2)_3]}{28(N_2)_3 + 32(O_2)_3} + \frac{u_3^2}{2} = c_1 = Rc_4 \quad (31)$$

This equation is written as though the quantities  $\beta$  are not functions of temperature. Reference 2 has a listing of the values of the various quantities  $\beta$  which shows that considering them constant gives a good approximation over the range of temperatures considered herein. The average values chosen for the present calculations are

$$\beta_{N_2} = 4.6$$

$$\beta_N = 2.7$$

$$\beta_{O_2} = 4.9$$

$$\beta_O = 2.6$$

Furthermore, the values given in reference 2 for the quantities  $\beta$  meet the specifications mentioned previously: they include the external work but do not include the energy that is used in dissociation. (Accordingly, the values of  $\beta$  do not need to be corrected for the different value of  $D_{N_2}$  used herein as compared with the value used in ref. 2.)

Because the rate equations contain only the concentrations and the temperature as variables (besides the independent variable  $t$ ), and because the flow equations must be solved simultaneously with the rate equations, the flow equations will be reduced to only two equations (the two following equations) in terms of the concentrations and the temperature. The equations of motion and of mass conservation can be combined. The quantity  $p$  is eliminated from equation (30) by means of the gas law (eq. (25)). Then,  $u$  is eliminated by means of equation (29). The quantities  $\bar{M}$  and  $\rho$  are eliminated by substitution of equations (26) and (27), respectively. The result is

$$\frac{R}{N_0} \left[ (N_2) + (N) + (O_2) + (O) \right] T + \frac{N_0 c_2^2}{28(N_2) + 14(N) + 32(O_2) + 16(O)} = c_3 \quad (32)$$

When  $u$  is eliminated from equation (31) by means of equation (29) and  $\rho$  is eliminated by equation (27), the result is

$$\frac{RT \left[ \beta_{N_2}(N_2) + \beta_N(N) + \beta_{O_2}(O_2) + \beta_O(O) \right]}{28(N_2) + 14(N) + 32(O_2) + 16(O)} + \frac{N_0^2 c_2^2}{2 \left[ 28(N_2) + 14(N) + 32(O_2) + 16(O) \right]^2} + \frac{D_{N_2}(N) + D_{O_2}(O)}{2 \left[ 28(N_2) + 14(N) + 32(O_2) + 16(O) \right]} = Rc_4 \quad (33)$$



## Solution of Equations

If equations (16) and (23) are combined to give the net rate of dissociation of oxygen, if  $(N_2)$  is eliminated by means of equation (28), and if equations (17) and (24) are combined to give the net rate of dissociation of nitrogen and  $(N_2)$  is again eliminated, then

$$\frac{d(O_2)}{dt} = - \left[ 29.9(O_2) + 18.1(O) + 1.6(N) \right] 1.15 \times 10^{-12} (O_2) T^{1/2} e^{-59400/T} +$$

$$\left[ 92.2(O_2) + 40(O) - 2.4(N) \right] 1.73 \times 10^{-36} (O)^2 T^{1/2} \quad (34)$$

and

$$\frac{1}{2} \frac{d(N)}{dt} = \left[ 21.4(O_2) + 12.4(O) + 3.8(N) \right] \left[ 3.76(O_2) + 1.88(O) - \right.$$

$$\left. 0.5(N) \right] 1.15 \times 10^{-12} T^{1/2} e^{-113340/T} -$$

$$\left[ 106.5(O_2) + 51.8(O) - 8.4(N) \right] 1.73 \times 10^{-36} (N)^2 T^{1/2} \quad (35)$$

If, furthermore,  $N_2$  is eliminated from equations (32) and (33) and numerical values are substituted for the constants, then

$$1.38 \times 10^{-16} \left[ 4.76(O_2) + 2.88(O) + 0.5(N) \right] T + \frac{6.02 \times 10^{23} c_2^2}{68.67 \left[ 2(O_2) + (O) \right]} = c_3 \quad (36)$$

and

$$\frac{22.2(O_2) + 11.2(O) + 0.4(N)}{68.67 \left[ 2(O_2) + (O) \right]} T + \frac{2.19 \times 10^{39} c_2^2}{\left\{ 68.67 \left[ 2(O_2) + (O) \right] \right\}^2} +$$

$$\frac{56,670(N) + 29,700(O)}{68.67 \left[ 2(O_2) + (O) \right]} = c_4 \quad (37)$$

For the actual process of computing the rates of dissociation, some simplifications were made. First, it was known that the dissociation of oxygen would be shown to be essentially completed before the dissociation of the nitrogen had hardly begun. Therefore, the computational procedure was simplified by computing separately the dissociation of the two gases. The dissociation of oxygen was carried through almost to completion. Then, with the final conditions for that process as the initial conditions for the dissociation of nitrogen, the computation of the dissociation process of nitrogen was carried out.

Second, it was known that, until the dissociation was close to equilibrium, recombination would have an entirely negligible effect on the net rate of dissociation. Therefore, the computations were greatly simplified by not using the last term in equations (34) and (35).

Furthermore, it was noticed that, because recombination was neglected, the variables could be so modified that the equations would be independent of the initial density of the air. The rate equations, equations (34) and (35), without their last terms were made independent of the initial density by dividing them by  $(O_2)_0^2$ , which is proportional to the square of the initial density; thus,

$$\frac{d \frac{(O_2)}{(O_2)_0}}{d \left[ \frac{(O_2)_0 t}{(O_2)_0} \right]} = - \left[ 29.9 \frac{(O_2)}{(O_2)_0} + 18.1 \frac{(O)}{(O_2)_0} + \right. \\ \left. 1.6 \frac{(N)}{(O_2)_0} \right] 1.15 \times 10^{-12} \frac{(O_2)}{(O_2)_0} T^{1/2} e^{-59400/T} \quad (38)$$

$$\frac{1}{2} \frac{d \frac{(N)}{(O_2)_0}}{d \left[ \frac{(O_2)_0 t}{(O_2)_0} \right]} = \left[ 21.4 \frac{(O_2)}{(O_2)_0} + 12.4 \frac{(O)}{(O_2)_0} + 3.8 \frac{(N)}{(O_2)_0} \right] \left[ 3.76 \frac{(O_2)}{(O_2)_0} + \right. \\ \left. 1.88 \frac{(O)}{(O_2)_0} - 0.5 \frac{(N)}{(O_2)_0} \right] 1.15 \times 10^{-12} T^{1/2} e^{-113340/T} \quad (39)$$

For the present computations, (N) in equation (38) and  $(O_2)$  in equation (39) were taken equal to zero.

The flow equations (eqs. (36) and (37)), in which both the concentrations and the constants  $c_2$  and  $c_3$  (but not  $c_4$ ) are proportional to the density, were made independent of the initial density in a similar manner; thus,

$$1.38 \times 10^{-16} \left[ 4.76 \frac{(O_2)}{(O_2)_o} + 2.88 \frac{(O)}{(O_2)_o} + 0.5 \frac{(N)}{(O_2)_o} \right] T + \frac{6.02 \times 10^{23} \frac{c_2^2}{(O_2)_o^2}}{68.67 \left[ 2 \frac{(O_2)}{(O_2)_o} + \frac{(O)}{(O_2)_o} \right]} = \frac{c_3}{(O_2)_o} \quad (40)$$

$$\frac{22.2 \frac{(O_2)}{(O_2)_o} + 11.2 \frac{(O)}{(O_2)_o} + 0.4 \frac{(N)}{(O_2)_o}}{68.67 \left[ 2 \frac{(O_2)}{(O_2)_o} + \frac{(O)}{(O_2)_o} \right]} T + \frac{2.19 \times 10^{39} \frac{c_2^2}{(O_2)_o^2}}{\left\{ 68.67 \left[ 2 \frac{(O_2)}{(O_2)_o} + \frac{(O)}{(O_2)_o} \right] \right\}^2} + \frac{56,670 \frac{(N)}{(O_2)_o} + 29,700 \frac{(O)}{(O_2)_o}}{68.67 \left[ 2 \frac{(O_2)}{(O_2)_o} + \frac{(O)}{(O_2)_o} \right]} = c_4 \quad (41)$$

In the actual calculations, the initial conditions were taken to be those at station (3). Thus,

$$(O_2)_o = (O_2)_3$$

Because of the aforementioned modifications to the equations, the results of the solution of the equations for a given value of  $T_o$  are applicable for all initial densities and can be shown by a single plot (for each  $T_o$ ) for all densities, with the following reservation being kept in mind. The recombination terms that were omitted from equations (38) and (39) are proportional to a higher power of the concentration than are the dissociation terms. Consequently, at high densities, equilibrium between the two rates occurs at a smaller degree of dissociation than at low densities. Therefore, at high densities,

dissociation does not continue until the concentration of  $O_2$  (or of  $N_2$ ) approaches zero. This reservation, that the results as calculated can be expected to become inaccurate at a value of the time parameter  $(O_2)_0 t$  that depends on the initial density, is discussed further in "Results and Discussion."

The computations consisted of a simultaneous solution of equations (38) (40), and (41) and a simultaneous solution of equations (39), (40), and (41). The computations were made on a modified Reeves Electronic Analog Computer. The uncertainty in the results due to analog-computer error is believed to be less than 5 percent.

In order to calculate the Mach number at station (4), where the dissociation of oxygen is complete, the speed of sound was taken as

$$a = \left( \frac{\bar{\gamma} RT}{\bar{M}} \right)^{1/2}$$

where  $\bar{M}$  is given by equation (26) and  $\bar{\gamma}$ , the average specific-heat ratio, is

$$\bar{\gamma} = \frac{\beta}{\beta - 1}$$

if the rate of change of degree of dissociation with density can be neglected, as it can be here. If the dissociation of oxygen is complete, then, by equation (28),

$$\begin{aligned} \bar{\gamma} &= \frac{\beta_{N_2}(N_2) + \beta_O(O)}{(\beta_{N_2} - 1)(N_2) + (\beta_O - 1)(O)} \\ &= \frac{\frac{79}{42} \beta_{N_2} + \beta_O}{\frac{79}{42}(\beta_{N_2} - 1) + (\beta_O - 1)} \end{aligned}$$

Therefore,

$$\bar{\gamma} = 1.35$$

and

$$a = 2,170 T^{1/2} \text{ cm/sec}$$

## RESULTS AND DISCUSSION

## Adjustment of Translation, Rotation, and Vibration

The results of the computations of the changes in the state of the gas due to the adjustment of translation, rotation, and vibration behind the shock wave are shown in table II for three values of the free-stream Mach number. Conditions behind the shock wave after adjustment of molecular translation and rotation were calculated by use of equations (1). Conditions after adjustment of molecular vibration were calculated by use of equations (5), (6), (9), and (10). The large drop in temperature due to the transfer of energy into vibration is to be noted.

The concentration of oxygen molecules after the completion of these adjustments  $(O_2)_3$ , which is taken as the initial concentration at the beginning of dissociation  $(O_2)_0$ , can be calculated for a given free-stream density by the equation

$$(O_2)_3 = 4.38 \times 10^{21} \frac{\rho_3}{\rho_2} \frac{\rho_2}{\rho_1} \rho_1$$

which was obtained from equations (27) and (28).

## Adjustment of Dissociation

The results of the computations of the dissociation process are shown in table II and figures 1 and 2. Figure 1 shows the course of the dissociation process of oxygen for three values of the temperature at station (3) (three values of the free-stream Mach number). The fact that the time rate of dissociation depends greatly on the temperature is clear from an examination of the change in the magnitude of the horizontal scales in figure 1 as the initial temperature is changed. The cooling of the gas due to dissociation is shown by the curves of  $T$ . The fact that the process takes place at nearly constant pressure is shown by the curves of pressure ratio. The increase in the density of the gas, due to cooling as dissociation proceeds, is shown by the curves of density ratio. The density ratio is less, however, than the inverse of the temperature ratio, because the molecular-weight ratio decreases as the degree of dissociation increases.

In figure 1(a), especially, the degree of dissociation at  $6.4 \times 10^{14} \frac{\text{molecule-sec}}{\text{cm}^3}$  is greater than might appear at first glance because of the density increase. The value of  $(O_2)/(O_2)_0$  is 72 percent, but the degree of dissociation of oxygen is not 100 - 72, or

28 percent; but, because the density has increased by the ratio 1.26, the degree of dissociation of oxygen is 100 - 57, or 43 percent.

Figure 2 shows the dissociation process of nitrogen for a free-stream Mach number of 14. (The conditions at  $t = 0$  in fig. 2 were obtained by extrapolation of the curves of fig. 1(c) to complete dissociation of oxygen.) The much lower speed of the dissociation process of nitrogen compared with that of oxygen is obvious from a comparison of the horizontal scales of figures 1(b) and 2 since both processes begin at approximately the same temperature.

The choice of variable for the horizontal coordinate of figures 1 and 2 implies that the results shown in these figures apply at all air densities, as they do with the following exceptions: In obtaining the results shown, the recombination process was neglected. Because the rate of recombination (the "rate" referred to is defined subsequently in this paragraph) is proportional to the density and the rate of dissociation is independent of the density, recombination at high densities cannot be neglected over the entire extent of the curves. The upper limit of the density for which the results as shown are applicable can be determined by comparing the rates of dissociation and recombination as given by the equations developed in the present paper for conditions at the right-hand end of the curves in the figures, and by determining the density at which the rate of recombination becomes as large as, for example, 10 percent of the rate of dissociation. In the comparison shown in table III, the rate of recombination of oxygen was divided by 6.8 for a temperature of 6,560° K, 8.1 for a temperature of 4,630° K, and 8.9 for a temperature of 3,450° K; and the rate of recombination of nitrogen was divided by 9 in order to make the ratio of the specific-rate constants agree with the equilibrium constant. (See the section entitled "Comparison of Equilibrium Constants.") The rates given for oxygen in table III refer to the absolute value of the quantity

$$\frac{d \frac{(O_2)}{(O_2)_0}}{d [(O_2)_0 t]}$$

and for nitrogen the rates refer to the absolute value of the quantity

$$\frac{\frac{1}{2} d \frac{(N)}{(O_2)_0}}{d [(O_2)_0 t]}$$

The limiting value of  $(O_2)_0$  is so chosen as to make the rate of recombination about one-tenth the rate of dissociation at the right-hand end

of the curves. The limiting density  $\rho_0$  (or  $\rho_3$ ) corresponds to the limiting concentration  $(O_2)_0$ , and the limiting density  $\rho_1$  is the free-stream density that results in the density  $\rho_0$  at station (3). The limiting altitude, the density altitude corresponding to the limiting  $\rho_1$ , was taken from table II of reference 20.

Another check on the upper limit of the density for which the full extent of the curves is applicable can be obtained from table 5 of reference 17 which gives the equilibrium composition of air as a function of pressure. The table is a rather rough approximation for the present application because it was calculated for equilibrium of both the oxygen and the nitrogen dissociations, whereas equilibrium was not reached in the present calculations nor, when the dissociation of oxygen was calculated, was the dissociation of nitrogen included. Nevertheless, use of table 5 of reference 17 gives estimated altitudes that are qualitatively in agreement with those shown in table III of the present paper.

The limiting altitudes shown in table III apply, as mentioned, at the ends of the curves (except for the bottom row of the table). The curves of figure 1 at smaller (less than full-scale) values on the horizontal axis would be applicable at lower altitudes (higher densities) because the slope of the  $(O_2)/(O_2)_0$  curve increases as the origin is approached, and the increased rate of dissociation may compensate for the increased rate of recombination that is due to the increased density.

The tentative tables for the upper atmosphere (ref. 20) show a change in the composition of air at high altitudes due to the dissociation of oxygen by solar radiation. The tables show complete dissociation of oxygen at altitudes above 100 kilometers in the day and above 120 kilometers at night, and partial dissociation down to 80 kilometers in the day and 105 kilometers at night. The present results should, therefore, not be expected to apply at altitudes high enough that a significantly large portion of the oxygen is originally in a dissociated state.

Figure 1 can be used to determine the distance behind the shock wave at which a moderate or a large portion of the oxygen is dissociated. For example, at a Mach number of 10 with  $(O_2)_0 t = 6.4 \times 10^{14}$ , the time  $t$  is 0.13 second for an altitude of 70,000 meters. For a local velocity of about  $4 \times 10^4$  cm/sec, the corresponding distance is about 5,000 centimeters. On the other hand, at a Mach number of 14 with  $(O_2)_0 t = 1 \times 10^{12}$ , the value of  $t$  is  $3 \times 10^{-6}$  second for an altitude of 35,000 meters. For a velocity of about  $5 \times 10^4$  cm/sec, the corresponding distance is 0.15 centimeter. These distances are, of course, in the undisturbed main stream behind a normal shock wave.

Figure 2 shows that the dissociation of nitrogen is very slow (compared with that of oxygen), and table III shows that appreciable dissociation of nitrogen occurs only at very small densities. For small densities, however, the time for appreciable dissociation to occur is large (compared with the length of a vehicle divided by the velocity of the air behind the shock wave). These facts fairly well establish (within the assumptions used in the present calculations) that the dissociation of nitrogen for flight at Mach numbers less than 14 at any altitude cannot proceed far enough to cause any significant effect on the properties of air and, therefore, will not produce any significant aerodynamic effect within the length of any conceivable vehicle.<sup>1</sup> (Referring to the entire length of a vehicle is being conservative, as expansions around corners would reduce the air temperature, the rate of dissociation, and the equilibrium degree of dissociation. Use of 300° K probably is also conservative, as ref. 21 shows measured values considerably below that.) This result is substantiated by the following examples: For  $(O_2)_0 t = 6.4 \times 10^{16}$  in figure 2, at the limiting altitude of 90,000 meters,  $(O_2)_0 = 3.5 \times 10^{14}$  and, therefore,  $t = 180$  seconds. Even for  $(O_2)_0 t = 0.064 \times 10^{16}$ ,  $t = 1.8$  seconds. Inasmuch as  $u \approx 5 \times 10^4$  cm/sec, the corresponding distance behind the shock wave is  $9 \times 10^4$  centimeters. At higher altitudes (higher than the limiting altitude) where  $(O_2)_0$  is smaller,  $t$  is greater. At lower altitudes, the results at  $(O_2)_0 t = 6.4 \times 10^{16}$  do not apply, but those at smaller values of  $(O_2)_0 t$  may apply. Consider, for example,  $(O_2)_0 t = 0.2 \times 10^{16}$ . (Below this value the degree of dissociation is certainly too small to have any important aerodynamic significance.) The results will be applied at the lowest altitude for which the recombination rate is not too large. In the bottom row of table III for nitrogen, the limiting value of  $(O_2)_0$  is determined to be  $4.4 \times 10^{16}$ . Therefore,  $t = 0.04$  second and  $tu = 2 \times 10^3$  centimeters. To recapitulate, at high and low altitudes the dissociation of nitrogen is too slow at Mach numbers less than 14 for a significant degree of dissociation to occur within the length of a vehicle.

One other condition for the dissociation of nitrogen should be considered. For flights at altitudes where the oxygen is completely dissociated by the sun's radiation (100,000 meters and above in the daytime), the dissociation of nitrogen will not be preceded by the thermal dissociation of oxygen (which causes a large drop in temperature) and, therefore, will occur at a higher temperature and at a greater rate. A simple

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<sup>1</sup>It should be stressed that this result does not necessarily apply for the slower flow in the boundary layer.



approximate calculation is made here to determine whether the rate is sufficiently increased that a significant degree of dissociation can occur within the length of a vehicle. The only change in the rate will be that due to increased temperature, because in both cases complete dissociation of oxygen occurs before the dissociation of nitrogen begins. The rate will, therefore, be increased by the product of the ratio of the square roots of the temperatures and the ratio of the Boltzmann factors. In one case, the initial temperature is  $T_3$  (equal to  $8,857^\circ \text{K}$ ), and, in the other, is  $T_4$  (equal to  $6,640^\circ \text{K}$ ). The initial rate is, therefore, increased by a factor of 142. The smallest value of  $(O_2)_0^t$  that is consistent with a reasonable degree of dissociation is about  $0.2 \times 10^{16}$  in figure 2. With the new rate, this value becomes approximately  $1.4 \times 10^{13}$ . At the lowest altitude (100,000 meters), the time is smallest (0.16 second). If  $u \approx 5 \times 10^4$  cm/sec, this time corresponds to a distance of about  $8 \times 10^3$  centimeters.

#### CONCLUDING REMARKS

The present calculations of the rate of dissociation of air have been based on available theory and available experimental results with other gases. The results of the calculations represent an extension of Bethe and Teller's work in that the present results follow the dissociation process from its initiation to the approach to equilibrium and in that they apply to a range of densities. The results show that the distance behind a normal shock wave required for a moderately large fraction of the oxygen to dissociate varies widely with Mach number and density, from approximately hundreds of meters to a fraction of a millimeter. The distance required for a significant portion of the nitrogen to dissociate (outside the boundary layer) is shown to be greater than the length of a vehicle at any density and at any Mach number less than 14.

Langley Aeronautical Laboratory,  
National Advisory Committee for Aeronautics,  
Langley Field, Va., January 3, 1956.

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TABLE I.- COMPARISON OF EQUILIBRIUM CONSTANTS

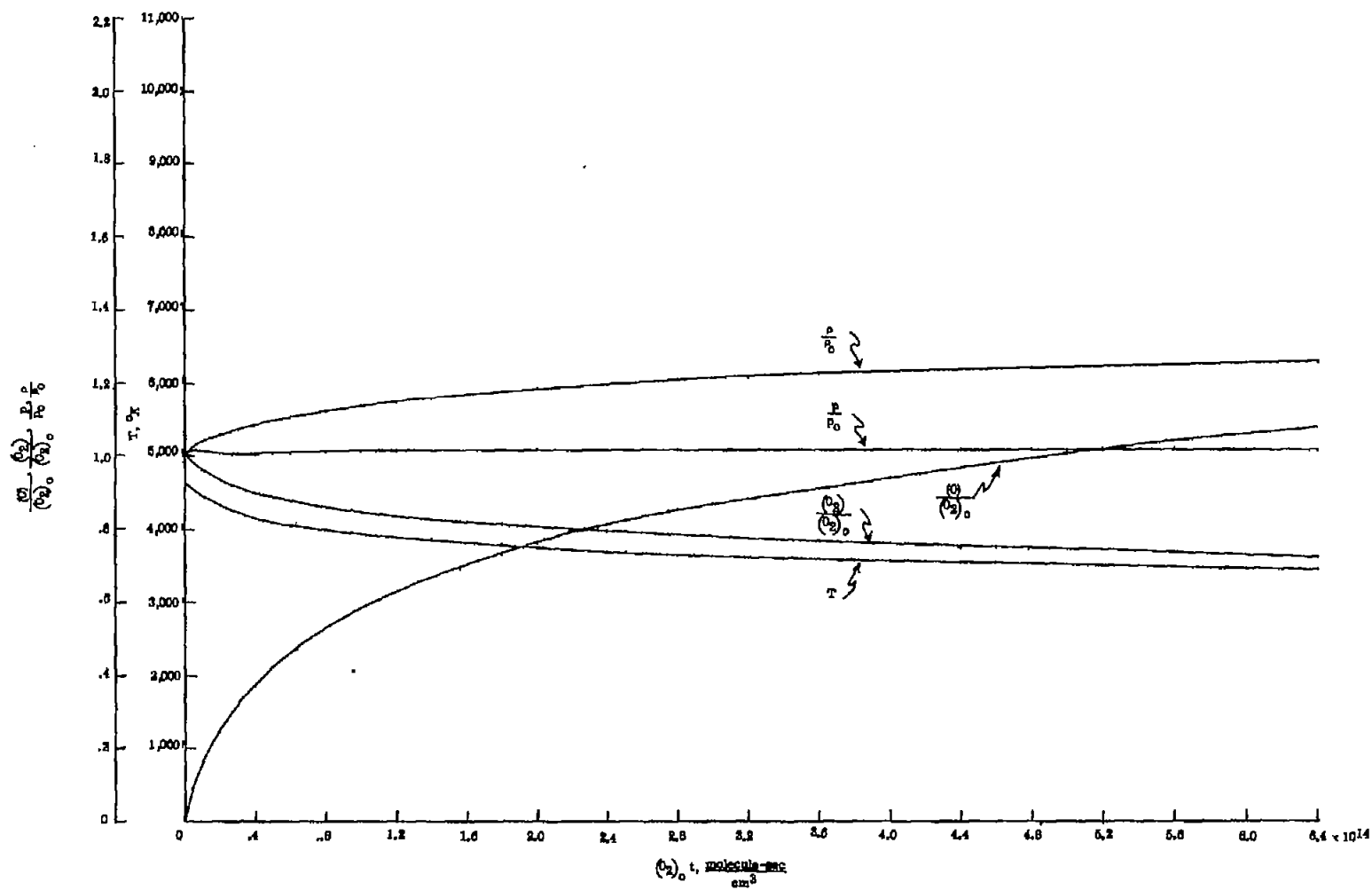
Temperature, °K	$K_p$ (from ratio of rate constants), atm	$K_p$ (from ref. 17, corrected), atm	Ratio of values of $K_p$
Oxygen			
4,000	0.2576	2.182	0.118
4,500	1.506	12.21	.123
5,000	6.270	48.42	.129
5,500	20.32	149.8	.136
6,000	54.49	384.8	.142
7,000	261.5	1,706	.153
8,000	863.2	5,258	.164
Nitrogen			
4,000	$3.285 \times 10^{-7}$	$3.087 \times 10^{-6}$	0.106
4,500	$8.609 \times 10^{-6}$	$7.936 \times 10^{-5}$	.109
5,000	$1.187 \times 10^{-4}$	$1.077 \times 10^{-3}$	.110
5,500	$1.025 \times 10^{-3}$	$9.198 \times 10^{-3}$	.111
6,000	$6.229 \times 10^{-3}$	$5.551 \times 10^{-2}$	.112
7,000	$1.080 \times 10^{-1}$	$9.629 \times 10^{-1}$	.112
8,000	$9.340 \times 10^{-1}$	8.503	.110

TABLE II.- CONDITIONS AT VARIOUS STATIONS

$T_1$ , °K	$M_{a,1}$	$u_1$ , cm/sec	$T_2$ , °K	$M_{a,2}$	$u_2$ , cm/sec	$\rho_2/\rho_1$	$p_2/p_1$	$T_3$ , °K	$M_{a,3}$	$u_3$ , cm/sec	$\rho_3/\rho_2$	$p_3/p_2$	$T_4$ , °K	$M_{a,4}$	$u_4$ , cm/sec	$\rho_4/\rho_3$	$p_4/p_3$	$\bar{M}_4/\bar{M}_3$
300	10	$3.5 \times 10^5$	6,116	0.39	$6.1 \times 10^4$	5.7	116	4,622	0.34	$4.4 \times 10^4$	1.4	1.06	---	---	---	---	---	---
300	12	4.2	8,683	.39	7.3	5.8	168	6,564	.34	5.2	1.4	1.06	4,100	0.32	$3.8 \times 10^4$	1.37	1.03	0.83
300	14	4.9	11,716	.38	8.4	5.8	228	8,857	.34	6.1	1.4	1.06	6,440	.30	5.2	1.18	1.03	.83

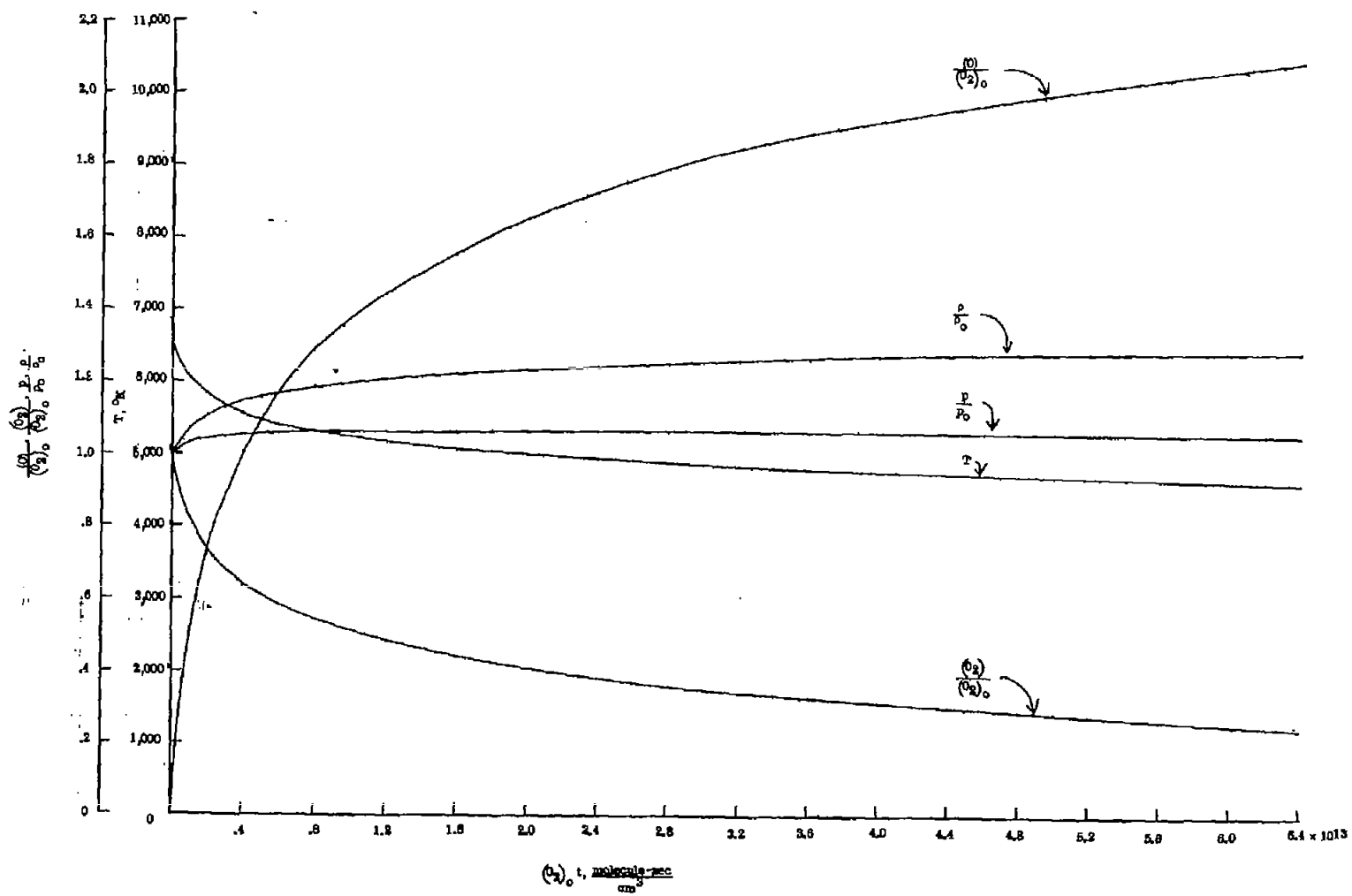
TABLE III.- DETERMINATION OF LIMITING ALTITUDE

$M_{a,1}$	$t(O_2)_0$	Rate of dissociation	Rate of recombination	Limiting value of $(O_2)_0$	Rate of recombination	Limiting initial density, $\rho_0$ , gm/cm <sup>3</sup>	Limiting free-stream density, $\rho_1$ , gm/cm <sup>3</sup>	Limiting altitude, meters
Oxygen								
10	$6.4 \times 10^{14}$	$6.8 \times 10^{-17}$	$1.4 \times 10^{-33} \times (O_2)_0$	$5 \times 10^{15}$	$7.0 \times 10^{-18}$	$1.1 \times 10^{-6}$	$1.4 \times 10^{-7}$	70,000
12	$6.4 \times 10^{13}$	$2.4 \times 10^{-15}$	$6.8 \times 10^{-33} \times (O_2)_0$	$4 \times 10^{16}$	$2.7 \times 10^{-16}$	$9.1 \times 10^{-6}$	$1.1 \times 10^{-6}$	48,500
14	$4.0 \times 10^{12}$	$2.9 \times 10^{-14}$	$9.4 \times 10^{-33} \times (O_2)_0$	$3 \times 10^{17}$	$2.8 \times 10^{-15}$	$6.8 \times 10^{-5}$	$8.4 \times 10^{-6}$	35,000
Nitrogen								
14	$6.4 \times 10^{16}$	$4.6 \times 10^{-18}$	$1.3 \times 10^{-33} \times (O_2)_0$	$3.5 \times 10^{14}$	$4.6 \times 10^{-19}$	$7.8 \times 10^{-8}$	$9.8 \times 10^{-9}$	90,000
14	$0.2 \times 10^{16}$	$6.2 \times 10^{-17}$	$1.4 \times 10^{-34} \times (O_2)_0$	$4.4 \times 10^{16}$	$6.2 \times 10^{-18}$	$1.0 \times 10^{-5}$	$1.3 \times 10^{-6}$	47,000



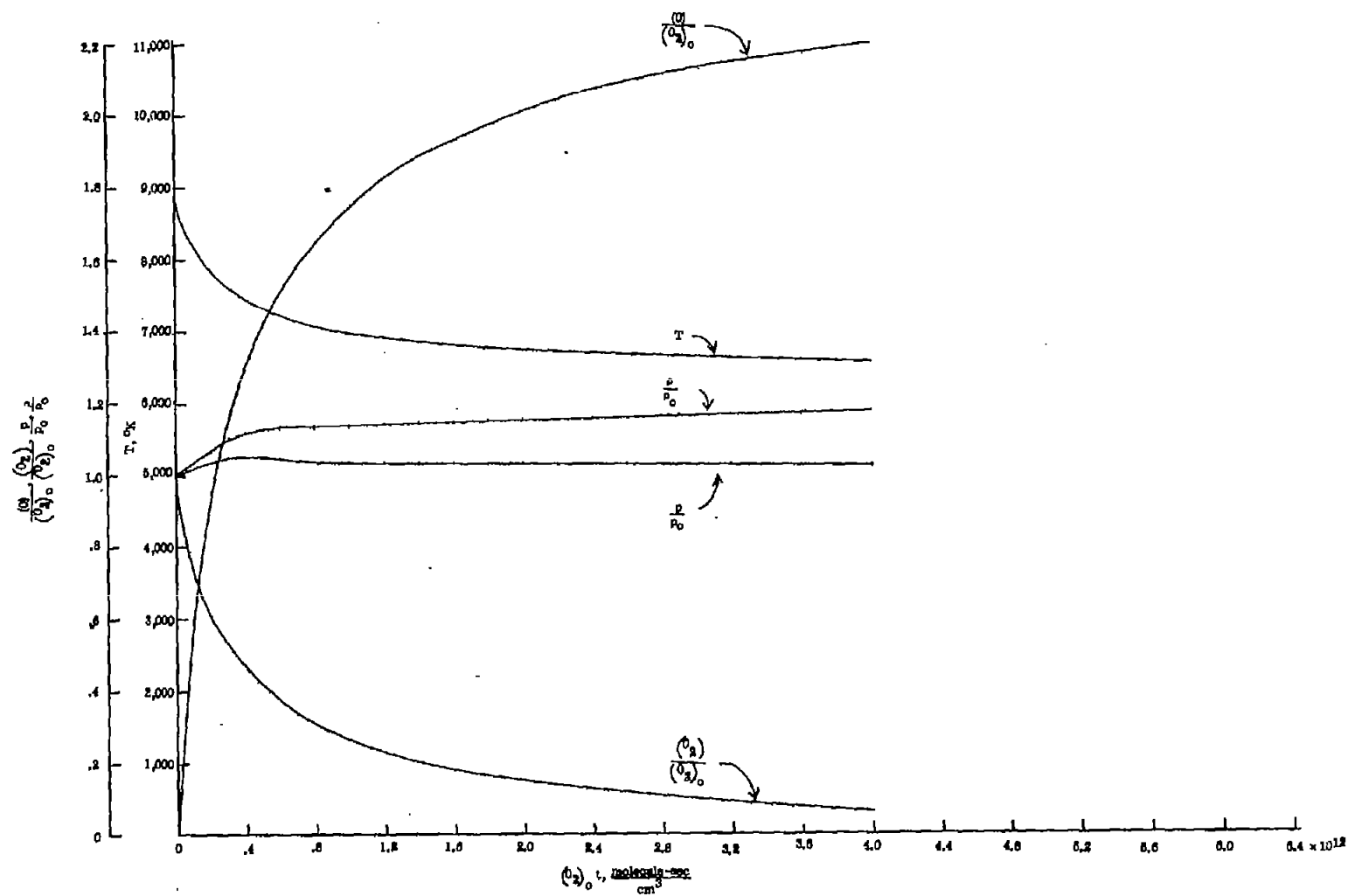
(a)  $N_{Ma,1} = 10$ .

Figure 1.- Dissociation of oxygen in air behind a normal shock wave.



(b)  $N_{Ma,1} = 12.$

Figure 1.- Continued.



(c)  $N_{Ma,1} = 14$ .

Figure 1.- Concluded.



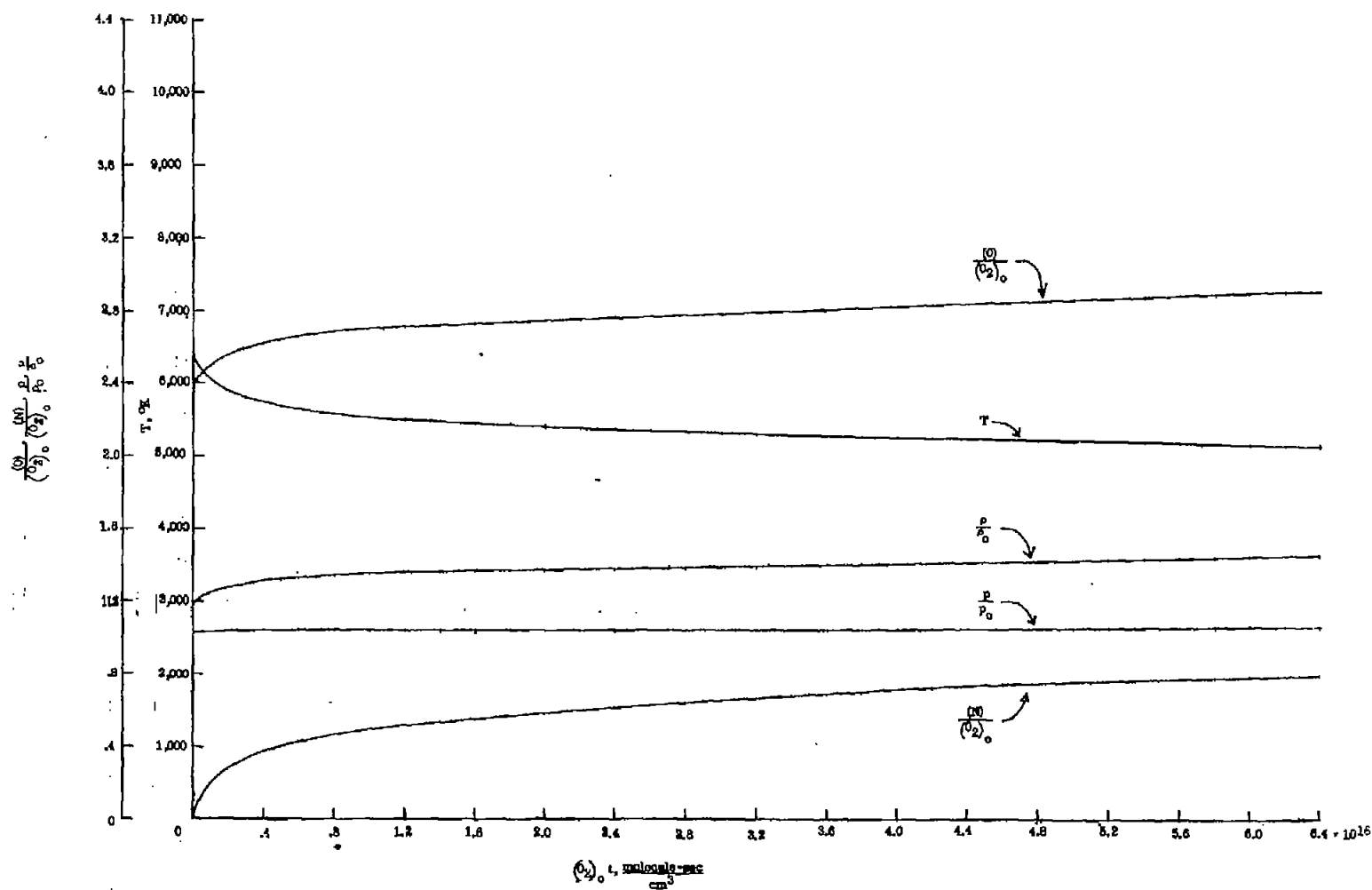


Figure 2.- Dissociation of nitrogen in air behind a normal shock wave.

$$N_{Ma,1} = 14.$$